ABSTRACT

CHEMISTRY

ARNOLD, SHANNON B.S., MOREHOUSE COLLEGE, 1992

MICROPHASE SEPARATED MIXED IONIC AND ELECTRONIC CONDUCTING BLOCK COPOLYMERS

Advisor: Dr. Ishrat M. Khan

Thesis dated February, 1995

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MICROPHASE SEPARATED MIXED (IONIC AND ELECTRONIC) CONDUCTING BLOCK COPOLYMERS

A THESIS

SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

By

SHANNON ARNOLD

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

MARCH 1995

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CHAPTER I

INTRODUCTION

1.1 Electroactive Polymers

The field of conducting polymers has produced much interest over the last fifteen years in an effort to supply a new class of materials. Inorganic materials exhibiting mixed electronic and ionic conductivities have been extensively studied.[1-4] These mixed conducting inorganic materials have found a wide range of applications in devices such as batteries, chemical sensors, and oxygen-permeable membranes.[5-6] Titanium disulfide and β-alumina are two such examples of inorganic materials used as cathodes in solid state batteries.[7-9] For any material to be an effective cathode material in a battery configuration, it must be a sink for the anode metal, possess high ionic mobility and high electronic conductivity. In these materials, the anode metal may rapidly diffuse into the Van der Waals layers as shown schematically in Figure 1 for TiS_2.

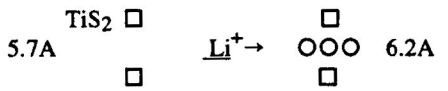


Figure 1.1

Organic polymers are finding wide use ,as well as, anticipated use in emerging technologies. Organic conducting polymers are also termed electroactive polymers. Electroactive polymers are divided into two areas 1) electronic conducting polymers-

polyacetylene is the most conductive doped polymer, yet this polymer is very intractable. Polythiophene and it's derivatives have found wide use due to processability, conductivity, and stability. 2) ionic conductive polymers which consist of poly (ethylene oxide) derivatives doped with alkali metal salts which provide the ion for transport. Organic conducting polymers are divided into three different classes for simplification, based on molecular structure: extended (-systems, pyrolytic polymers, and charge-transfer systems.11 Electronic conducting polymers commonly contain extended (conjugated) π-systems, chains of alternating single and double bonds, aromatic rings or heteroaromatic rings. Upon appropriate doping these polymers are oxidized or reduced. The resulting charges (electrons or holes) are delocalized along the chain. Ionic conducting polymers are prepared by dissolving salts in polymers capable of coordinating ions. The segmental motion of the polymer chain is instrumental in ion movement in the polymer matrix and this results in ionic conductivity. Electroactive polymers have a number of applications to include use as electrolytes and electrodes in high energy density storage devices, biomembranes, aerospace applications, photoelectrochemical displays, electrochemical displays, actuators, sensors, and electromagnetic interference shields.[9-17] Because solid polymer electrolyte based devices have higher energy density (> 100 W dm-3), longer shelf and cycle life, fewer sealing problems, and more convenient fabrication for utilization in microelectronic devices[9,14] there is considerable interest in the design and synthesis of electroactive polymers (electronic and ionic). In the area of polymeric materials, the design and synthesis of novel electroactive polymers has been limited to either purely electronic conductive or purely ionic conductive polymers.[9,18] Novack and coworkers

electronic conductive or purely ionic conductive polymers.[9,18] Novack and coworkers reported the preparation of electroactive blends of poly(pyrrole) and poly(ethylene oxide)/alkali metal salts. These blends have demonstrated enhanced coulombic capacity of the electrode because of the close contact between the poly(pyrrole) [*electrode*] and poly(ethylene oxide)/alkali metal salt [*electrolyte*]. However, because of the heterophase (macroheterogeneity with phases in the micron range) of the blends, ion diffusion is hindered. A single polymeric material combining both electronic and ionic conducting properties may be expected to show certain advantages, since ion diffusion would be less hindered with a microheterogeneous (100 to 300 angstrom microdomain sizes) polymer matrix. In this regard appropriately doped poly[N-(3,6,9-trioxadecyl)pyrrole], abbreviated as poly(NTP), with an electron conducting backbone and an ionic conducting side chain has been prepared.[19] This polymer backbone can be doped with electron donors or acceptors, while the side chain can be doped with alkali metal salts to yield electronic and ionic conductivity, respectively. The coulombic capacity of this polymer was greatly improved relative to the parent poly(pyrrole) and was attributed to the better interpenetration of the electrolyte into the electroactive material. Better discharge characteristics were also exhibited, presumably because of the reduction of the ionic resistance. However, this (NTP) has not been demonstrated to be microheterogeneous i.e. discrete and well defined separate electronic and ionic phases are not present. The resulting characteristic of this polymer is high impedance or limited charge transport in the electrode. The problem of limited charge transport may be overcome by design and synthesis of a polymer incorporating two separate conducting microphases (ionic and

electronic). This polymer would consist of an electronically conducting block being covalently linked to an ionic conductive block. A polymeric material of this type would be beneficial in three ways. It could be totally electronic conducting, totally ionic conducting, or ionic and electronic conducting simultaneously. In 1991 Li and Khan first reported an entirely new concept in the area of electroactive polymers known as microphase separated mixed ionic and electronic conductive (MIEC) block copolymers.[20-21] Initially, a series of poly[ω-methoxyocta(oxyethylene)methacrylate-block-4-vinylpyridine][22] and poly[3-methylthiophene-block-ω-methoxyocta(oxyethylene)methacrylate] block copolymers were synthesized. The p[MG8-B-4VP] copolymer was doped with LiClO4 to obtain an ionic conducting oligooxyethylene domain, while the 4-vinylpyridine block was doped with 7,7,8,8-tetracynoquinodimethane (TCNQ) to obtain an electronic conductive phase. The p[3MT-B-MG8] copolymers were converted to MIEC polymeric materials by appropriate doping with I_2 (electronic) and $LiClO_4$.[21] Each of these copolymer/dopant systems are microphase separated with electronic and ionic conductivities limited to separate microdomains. The block copolymer 4-vinylpyridine-block-MG8 was found to have low conductivity values in the ionic (10^{-6} S cm^{-1}) and electronic (10^{-6} S $cm^{-1)}$ domain.[22] In an effort to increase conductivity values, a copolymer of 3-methylthiophene-block-MG8 was synthesized giving ionic (10^{-6} S cm^{-1}) and electronic (10^{-3} S cm^{-1}) conductance values.[12,21] In this thesis, design, synthesis, characterization, and properties of a third series of polymers poly[(3-octylthiophene-co-3-methylthiophene-block-ω-methoxyocta(oxyethylene)methacrylate)] will be reported on. These polymers represent a new concept in the area of electroactive polymers and have potential to lead to major

switches, sensors, elastomeric polymer electrodes, biomembranes capable of electron/ion transfer, and electromagnetic radiation shields. Furthermore, these polymers may be considered as polymeric counterparts of TiS_2 and V_6O_{13} cation insertion materials.[7-8,10]

Morphologies of the block copolymers are determined by weight fractions of the electronic to ionic phases, different morphologies are possible for these block copolymers. In Figure 1.2 two idealized morphologies are depicted. Figure 1.2 (a) depicts cylindrical electronic phases immersed in an ionic conductive matrix and (b) is a lamallae morphology with an electronic conducting layer and an ionic conducting layer. The MIEC block copolymers described herein exhibit enhanced electroactive properties,and the ability to be melt processed which makes them attractive for applications.

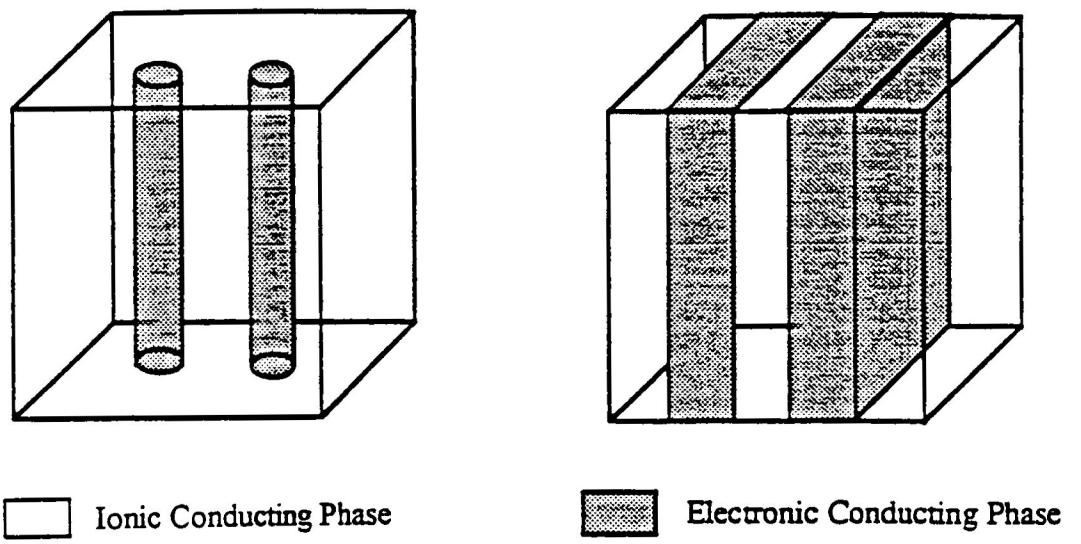


Figure 1.2 Idealized Morphologies of Microphase Separated MIEC Block Copolymers.

1.2 Objectives

The objectives of this thesis project are: (1) the synthesis and characterization of microphase separated mixed (electronic and ionic) conducting block copolymers (2) optimization of conductive properties of the polymers.

These objectives were accomplished by conducting the following tasks:

i. Synthesis of Octylthiophene.

ii. Purification of monomers using high vacuum techniques.

iii. Synthesis of Additional Grignard reagents.

iv. Synthesis of poly[3-octylthiophene-co-3-methylthiophene-block-ω-methhoxyocta(oxyethylene)methacrylate] by cross-coupling polymerization and ionic polymerization.

v. Characterization of all polymer systems.

1.3 Scope of the work

Chapter II contains the theoretical background information associated with the current project. First, a condensed background of the conductivity of organic materials is presented. A background of several important classes of electronic conducting polymers is included, along with performance properties observed since the 1970's with the discovery of polyacetylene, the most conductive doped polymer. A new system of organic mixed (ionic and electronic) conducting material is also described.

Chapter III includes experimental procedures, reagents, and apparatus used tocarry out this work. All of the synthetic procedures are described in detail. The procedures for general characterization such as NMR, TGA, DSC, GC-MS, and TEM are briefly

described. The aspects of conductivity measurement, including theory fundamental techniques and specific apparatus are addressed in detail in this section.[12] Chapter IV includes results, data analysis and discussions. Major emphasis is placed on optimization of conductivity properties, processability, and stability of these new electroactive polymeric materials. To understand the mechanism of conductance of these polymeric materials, a microstructure model is being proposed.

CHAPTER II

BACKGROUND

2.1.1 Aspects of Conductivity in Organic Materials

Based on electrical conductivity all materials are classified as conductors (metals), semiconductors, and insulators. In the attempt to develop an understanding for charge transfer within solids a model was developed based on band theory.[11,30,31] Many other theories have been proposed in order to gain insight into the occurrence of electrical conduction in organic materials.[24-27,32] Of these, band theory has been established as the basis for understanding the distinction between insulators, semiconductors, and metallic conductors.

Atoms and molecules in isolation exhibit quantized electron energy levels, i.e. electrons in the atom may exist in one of several discrete energy levels associated with the atom. Electrons occupy energy levels (orbitals) which may contain one electron, two electrons of opposite spin, or they may be empty. The electrons are allowed to undergo transitions about the levels, under the appropriate conditions. Yet, they are forbidden to attain energies that are outside of the quantized energy levels. In crystalline solids, energy levels broaden into energy bands, as shown in Figure 2.1.1. The bands actually consist of n very closely-spaced energy levels, where n is the number of atoms in the crystal. These levels are so closely spaced that they effectively form a continuum, and are described by a

density of states. Depending upon the state of occupation of these bands different electronic behavior is achieved in a solid. If an electric field is applied in the presence of an electron, the electron will experience a force. The electron gains energy and becomes part of an electric current within a solid. The electron as stated before due to quantization can sufficient energy to accelerate to next the highest unoccupied energy level. If there is no such level, the electron is forbidden to accelerate, and there is noelectrical conduction.[11]

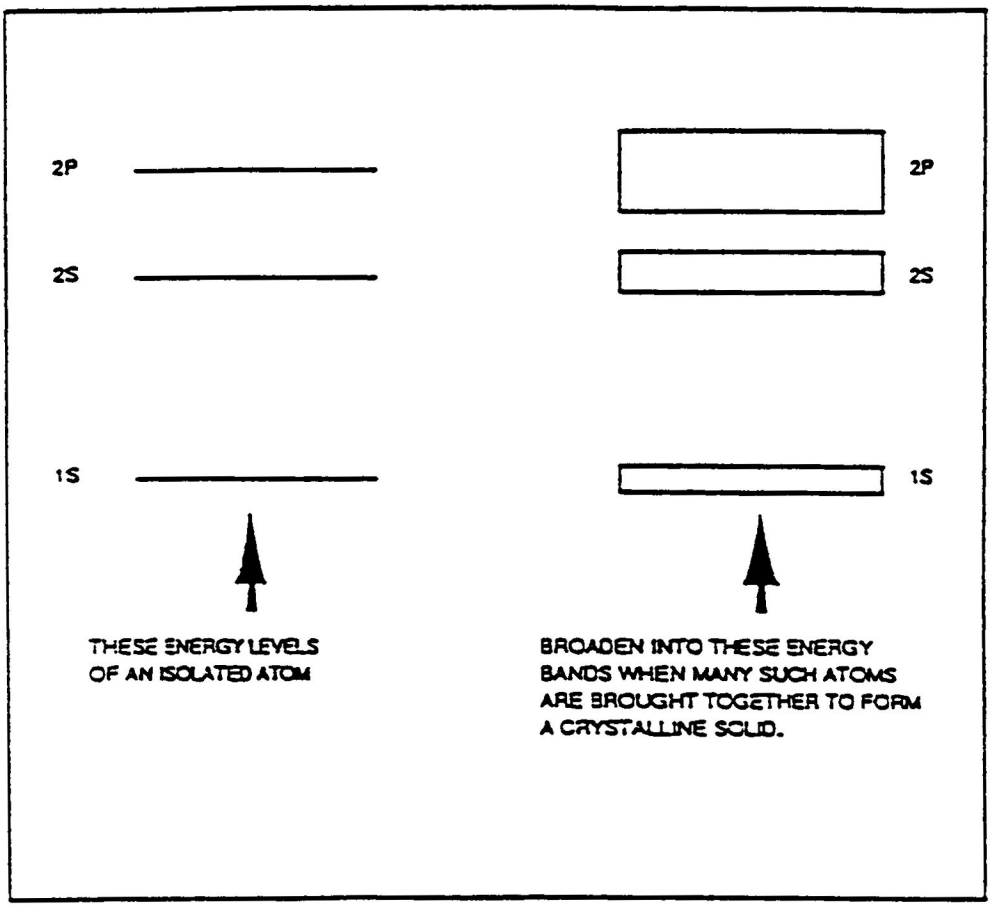


Figure 2.1.1 Energy bands in solids

An explanation for insulators has been given by viewing a solid consisting of two bands, as shown in Figure 2.1.2. The bottom of the conduction band and the top of the valence band are separated by a large energy gap Eg. The valence band is completely filled with electrons, and the conduction band is empty. In the case of the conduction band being empty, when an electric field is applied most of the electrons from the valence band have no unoccupied energy levels directly above them, and do not move in response to the field. However, the electrons at the top of the valence band do have empty levels (conduction band) above them, except they must overcome the energy gap in order to occupy these levels. The electrons can obtain sufficient energy for crossing the Eg from the electric field being applied or by thermal excitation through a process known as lattice vibration. In the event that the gap is large then almost none of the electrons will gain enough energy to undergo transition to the next level, thus no electronic conduction occurs. Materials possessing a very large energy gap separating an empty conductive band from a filled valence band, are known as insulators. Insulators normally have an Eg on the order of 10 eV.

The solid labeled as 2B pictured in Figure 2.1.2, has a filled valence band and a partially filled conduction band. The highest occupied level of the conduction band is called the Fermi energy Ef. When an external field is applied, electrons near the Fermi energy have unoccupied levels directly above them. These electrons may undergo transition in response to the applied field and participate in electrical conduction. These materials are known as conductors.

A semiconductor can best be described as an insulator with an Eg that is smaller by an order of magnitude.[11] Due to the smaller energy gap electrons can be excited across into the conduction band. Once the energy gap is crossed electrical conduction can take place by the same mechanism observed in metallic conductors. When the electron undergoes transition across the energy gap, it creates a hole in the valence band. Thenewly generated hole is now a positively-charged carrier. Electric conduction in a semiconductors involves charge transfer by both electrons and holes.

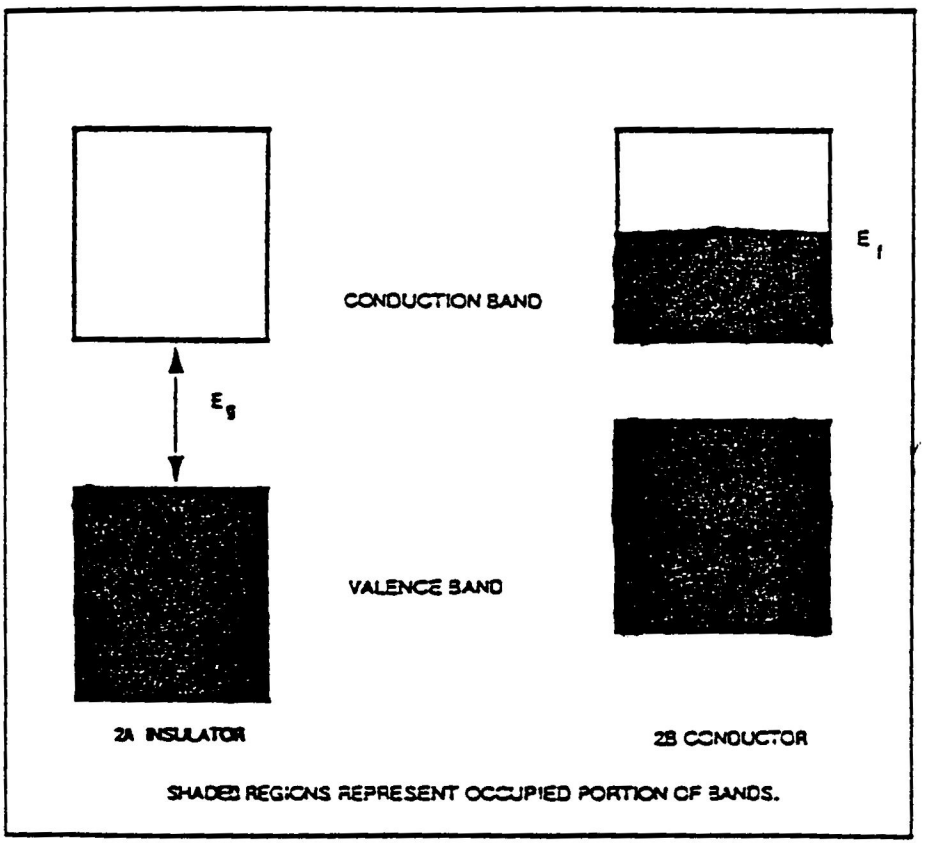


Figure 2.1.2 Electronic occupation of conduction and valence bands

Polymers and organic conducting materials generally have molecular structures which are disordered. Thus, most polymers are insulators initially, yet some polymers can be made conductive by selective synthesis or by proper doping with electron donors/acceptor groups see Figure 2.1.3. Organic conductors have been divided into three classes: extended π-systems, pyrolytic polymers, and charge transfer systems.

Conducting polymers based on an extended π-system consist of chains of alternating single and double bonds, aromaticrings or heteroaromatic rings. These "unsaturated systems" can be extended into a linear conjugated array of bonds. An example would be polyacetylene, which contains many orbitals. These orbitals form dense conduction and valence bands. Neutral polyacetylene is an insulator because its energy gap is large. Upon n-type doping, an electron from the dopant is transferred into the polymer conduction band, a polaron in association with the counter ion M+ is formed, accompanied by the generation of a doubly occupied bonding orbital (valence band) and a singly occupied anti-bonding orbital (conducting band). As the doping level increases, in the polymer more polarons are formed. Polarons interact with each other electronically producing a new charge carrier called a bipolaron. This phenomena is depicted in Figure 2.1.4. Partial oxidation (p-doping), electron is removed from the valence band, or reduction (n-doping) of the polymer occurs. The resulting charge is delocalized along the chain, by rearrangement of the single and double bonds in the conjugated system for both dopants types. The bipolaron model is also used for the description of the hopping process of the charge carriers between adjacent polymer chains, as shown in Figure 2.1.5.[30]

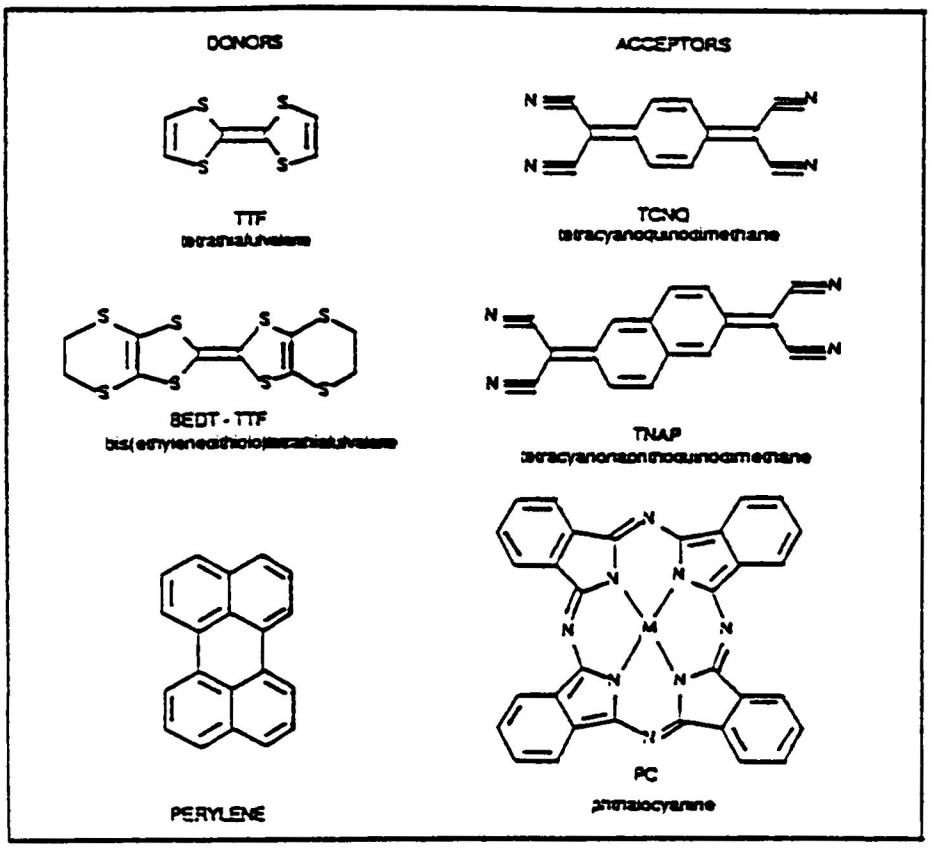


Figure 2.1.3 Examples of Organic donors and acceptors

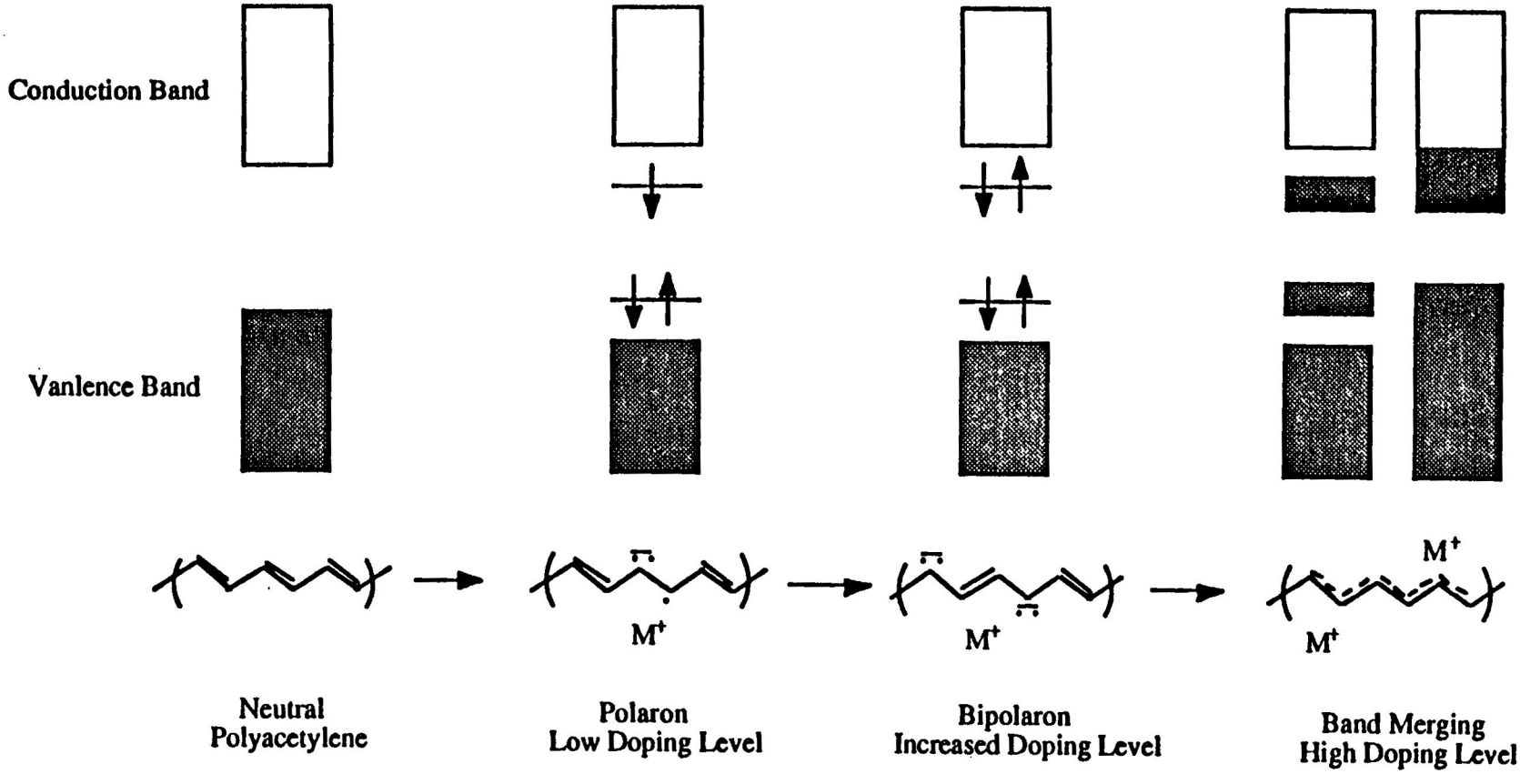


Figure 2.1.4 Band Structure of n-Doping Polyacetylene

It is generally accepted that due to the high activation barrier this inter-chain hopping is the rate limiting process for the charge transfer that occurs in the conjugated system. Through combined intra- and inter-chain charge transfer, electrical conduction is evident in conjugated organic polymers. The observed conductivity, σ can be expressed as

$$\sigma = \sigma_h + \sigma_o$$

where σ_h is the hopping conductivity and $\sigma_o$is the intrachain conductivity.

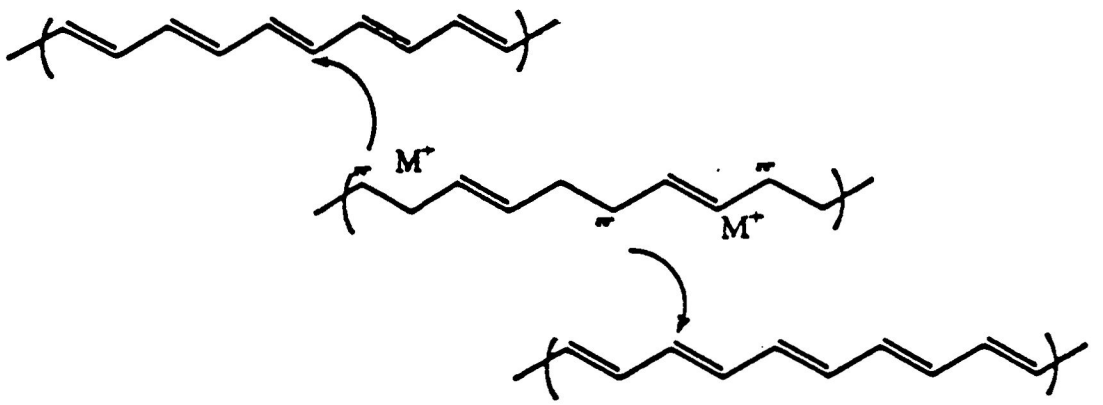


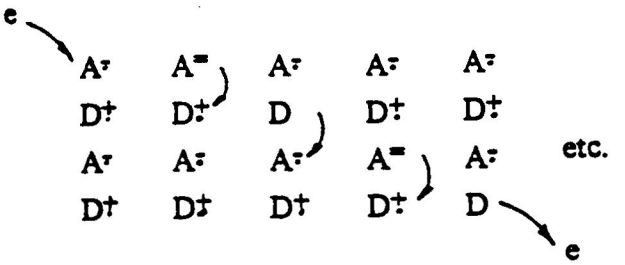
Figure 2.1.5 Interchain Hopping of Bipolarons in a Conjugated System

In addition to conjugated polymeric systems, there are several rather special classes of organic compounds which show high electronic conductivity. The most notable are charge-transfer complexes and radical ion systems. Charge transfer complexes are formed by partial transfer of an electron from a donor molecule of low ionization potential to an acceptor molecule of high electron affinity.

$$D + A \rightarrow D^{\delta+} + A^{\delta-}$$

(D: electron donor, A: electron acceptor)

The conductivity then occurs by radical-ion disproportionation



Usually, polymeric charge-transfer complexes are quite brittle materials and can therefore only be used where mechanical properties are not important. Nevertheless, one such material, poly(2-vinylpyridine)-iodine, has found commercial use in high efficient solid state batteries.[33]

2.1.2 Organic Polymeric Conductor

Electrically conducting polymers may be grouped into several classes:

(1). π-conjugated polymers

(2). Charge-transfer complexes

(3). metal-coordination polymers

(4). pyrolytic polymers

Figure 2.1.5 to Figure 2.1.8. give some examples of these various class of conducting polymers.

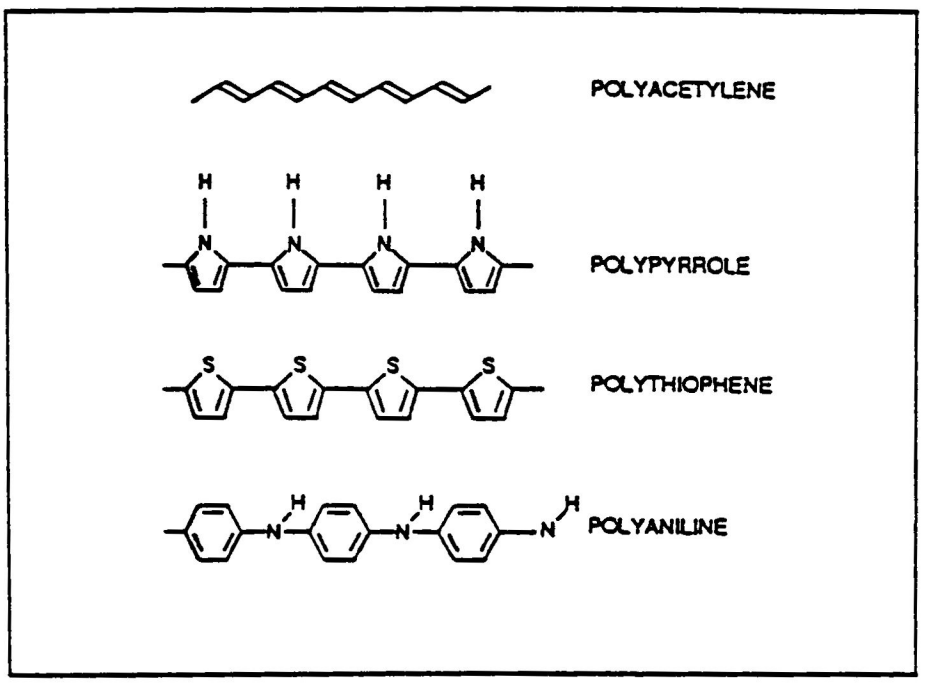


Figure 2.1.5 Examples of Extended π-systems

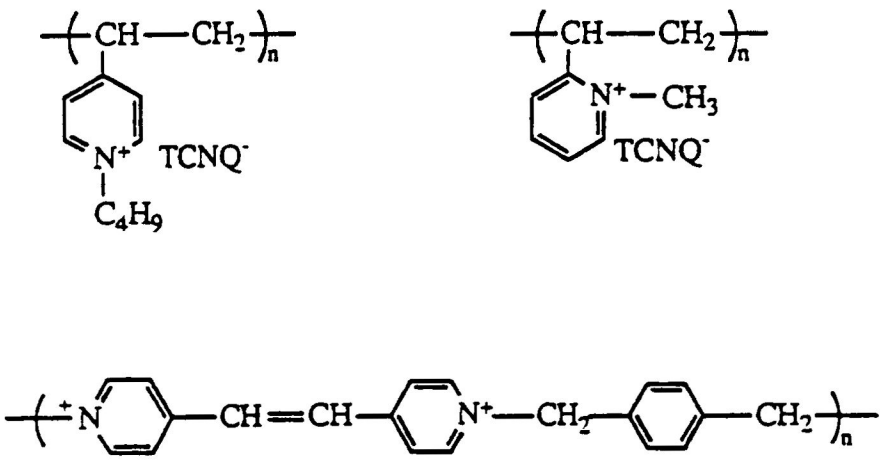
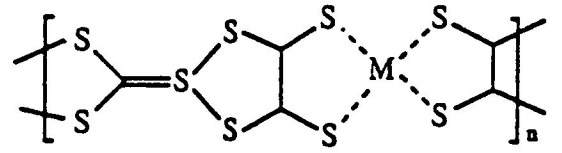
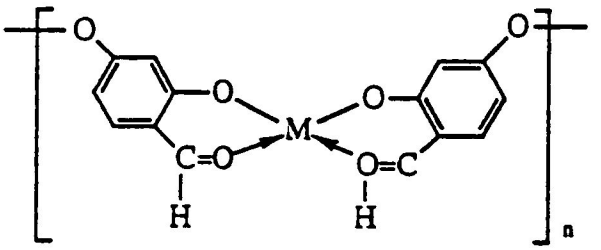


Figure 2.1.6 Examples of Polycation Anion Radial Salt



M= Ni, Cu, Pt



M= Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

III Metal-Containing Polymer

Figure 2.1.7 Examples of Metal-Containing Polymers

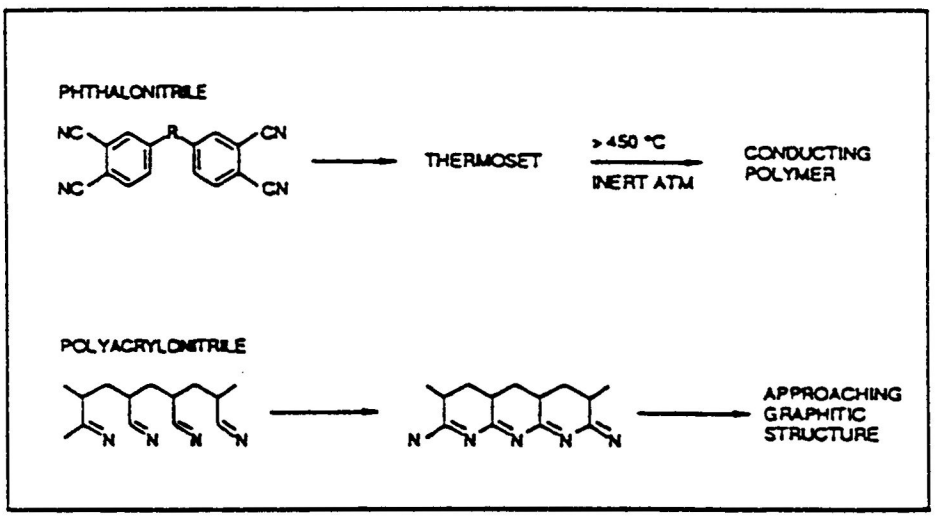


Figure 2.1.8 Examples of Pyrolytic (High Char Yielding) Polymers

1. π-Conjugated Polymers

π-Conjugated systems are the major class of organic conducting polymers. These systems have backbones consisting of alternating single and double bonds, which can delocalize electrons over all the atoms of the molecule. Polymers are generally insulators until appropriate doping occurs. Some of the π-conjugated polymers become highly conducting materials.

Polyacetylene is the most extensively studied conjugated conducting polymer due to its simple molecular structure. In 1977, it was discovered that the conductivity of polyacetylene film could be raised by nine orders of magnitude by chemical p-doping or n-doping. Conductivity also is dependent on the degree of defects (sp^3 carbon units) in the polymer chains. Defects can lead to scattering and localization of electron transport. A recent synthesis of highly oriented polyacetylene was doped to give much higher conductivity than before (within the copper range).[36-37] Furthermore, a study was conducted where controlled introduction of sp^3 carbon defects in polyacetylene demonstrated that the amount of defects correlated with significant changes in the electronic structure of the doped polymer.[35] The conductivities of doped polyacetylene typically ranges from 10^{-4} S cm^{-1} to 10^5 S cm^{-1} depending on the dopant used. Dopants are generally electron accepting (p-type), such as halogens (I_2), metal halides ($FeCl_3$), protonic acid or electron donating (n-type), such as tetrathiafulvalene, and sodium naphthalide. These polymers have some problems with environmental stability, processability, and moisture sensitivity. As a result, study of these polymers and their usefulness in applications has become a challenge.

In the last fifteen years heteroaromatic, and aromatic polymers have been studied . Polypyrrole and polythiophene have probably received the most attention. These polymers are hydrolytically and thermally stable. Poly(thiophene) has an extended conjugation which makes the polymer chain stiff, and much like a rigid rod polymer. As a

consequence the polymer can not be dissolved or melt processed. The solubility and conductivity of these polymers have been enhanced by introduction of aliphatic side chains.[38-43,83-85] As a result, polymer can be studied and made use of in application materials. Poly(3-alkylthiophene) derivatives are attracting the most attention. These macromolecules have been dissolved and melt processed. More recently, devices have been designed and suggested incorporating poly(3-alkylthiophenes).[43-44,86-89]

The processability of poly(thiophene) can be facilatated by blending with polymers such as poly(vinyl alcohol) and poly(vinyl chloride).[45] Conductive polymer composites of such systems have been prepared by blending with polystyrene in solution and casting films. These blend systems may serve to provide better processing properties and mechanical properties. Yet, their are drawbacks associated due to heterogeneity of mixing to different components and in some cases lack of solution processability due to the prescence of the insoluble polymer component. Copolymerization of poly(3-methylthiophene) with conventional polymers such as methylmethacrylate provides a new approach in making procesable conducting polymers.[46-47] These copolymers are soluble in several organic solvents and exhibit conductivities between 10^{-5} and 0.2 S cm^{-1}.

Poly(3-alkylthiophenes), like other conducting polymers conduct only when doped. The common doping methods include solution doping , vapor phase doing, and electrochemical doping. Sato et. al. [48] reported conductivities of 450 to 510 S cm^{-1} for poly(3-methylthiophene), synthesized by Grignard coupling polymerization at very high iodine concentrations. McCullough et. al.[49] reported on poly(3-alkylthiophenes) consisting of aliphatic butyl to dodecyl functionalities, describing conductivity values from 10^{-1} to 103 S cm^{-1}.

2.) Charge-transfer complexes

Organic conducting materials can achieve electrical conductivity through transfer of an electron, or charge, from an electron donor to an electron acceptor molecule see

(Figure 2.1.6.). These organic conductors are known as charge-transfer complexes. The first c-t salt was an electron acceptor, 7,7,8,8-tetracynoquinodimethane (TCNQ). The salt was synthesized by Beechgard.[50] The salt was originally believed to be semiconducting. However, in 1972 Cowan and coworkers[51], found that crystals of tetrathiafulvalene-tetracyanobenzoquinone (TTF-TCNQ), show metal-like conductivity. Several other charge-transfer salts have been synthesized. These donor and acceptor salts, generally are planar molecules with extended π-networks.

Charge transfer occurs when electron from the HOMO (Highest Occupied Molecular Orbital) of the donor are transferred to the LUMO (Lowest Unoccupied Molecular Orbital) of the acceptor. A very regular crystal is necessary to give optimal orbital overlap for charge transferring to occur. In the solid state, charge salts generally crystallize into two segragated stacks: one of all donor molecules, and the other comprised of all acceptor molecules. In each stack the orbitals form a band of electronic states. Charge transfer of some of the electrons gives rise to the partially filled bands needed for conduction. Conduction occurs anisotropically along these stacks.[52] Most charge transfer salts are incorporated as pendant groups on the polymer.[53-56]

Almost all charge transfer polymers are photoconductive, so conductivity can be enhanced as a function of electromagnetic radiation wavelength.[57]

3.) Metal Insertion Polymers

Metal Insertion Polymers have been incorporated into polymers. Metals in polymers work in several ways to improve electrical conductivity. The d-orbitals of metals may overlap with π-orbitals of the organic structure and delocalize electrons along a molecule. Metals may also serve as bridges in adjacent layers of polymers that stack to form a one dimensional system along the stacking direction. Most of these systems are insoluble and oligomeric, having poor conductivities, even which doped. Some

coordination polymers containing Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} show semiconductors properties with conductivities in the order of 10^{-10} to 10^{-6} S cm-1.

4.) Pyrolytic Polymers

Conductive polymers derived from pyrolysis of high char yielding polymers are termed pyrolytic polymers. Examples are seen in Figure 2.1.8. Most of the structures are carbon fibers designed from inceneration of polyacrylonitrile resins after spinning into fibers. These fibers are capable of conduction as high as 102 or 103 S cm-1.[61-65]

Phthalonitriles are the most promising of these polymers under current investigation.[66-67] These materials are thermosets so they are very stable to enviroment and moisture. However, the materials are inherently brittle and difficult to process due to a high degree of crosslinking.

2.1.3 Mixed Ionic and Electronic Conductors

Mixed ionic and electronic conductors have been extensively explored on inorganic materials such as flourite and pyrochlore compounds.[68-70] In mixed inorgancic conductors both ionic and electronic conductivities are generated in three ways: (a) thermal excitation, (b) deviation from stoichiometry, and (c) doping.[71] The classes of inorganic compounds have been found to exhibit fairly high conductivities. Tuller reported that pyrochlore compund Zr1-xYxO2-x/2, exhibits an ionic conductivity ~ 10^{-1} S cm^{-1} at 1000° C with a broad electrolytic regime.[69]

As there is no interface between the electrolyte and electrode in a mixed electronic and ionic conductor, the usual problem of overpotential due to a charge transfer across a phase boundary at an ion conductor-electrode interface is eliminated. The problem of chemical and thermal compatibility between an ion conductor and a separed electrode is such as solid oxide fuel cells, batteries, chemical sensors, and oxygen permeable membranes.[70]

The first organic composite of polymer electrolytes with polymer electrodes in secondary batteries was reported in 1981 by Chiang.[71]

CHAPTER III

EXPERIMENTAL SECTION

3.1 Polymerization of Poly[3-Octylthiophene-co-3-Methylthiophene-block-ω-methoxyocta(oxyethylene)methacrylate]

A chemical method for polymerization of poly[3-Octylthiophene-co-3-Methylthiophene-block-ω-methoxyocta(oxyethylene)methacrylate], abbreviated as P[3OT,3MT-B-MG8], is shown in scheme one. High vacuum line (10^{-3} ~ 10^{-5} torr) and breakseal techniques are required for purification of MG8 macromonomer. The polymer is synthesized via Grignard coupling between 5-iodo-3-methyl-2-thienylmagnesium iodide and 5-iodo-3-octyl-2-thienylmagnesium iodide, using a NiCl2(dppp) nickel chloride-phosphine complex catalyst.[73,74] The copolymerization occurs via opening breakseal of macromonomer MG8 which is initiated by Grignard polymerization, and reflux.

Synthesis of 2,5 Diiodo-3-Methylthiophene

2,5-Diiodo-3-Methylthiophene (DIMT) was prepared by iodination of 3-methylthiophene in CH2Cl2 using a 1:1 mixture of concentrated nitric acid and water as a catalyst as described by method of Barker et. al. in 1979.75 A 10 g solution (0.102 mol) of 3-methylthiophene (Aldrich 98%) in 350 ml of CH_2Cl_2 was placed in a 500 ml three necked flask , to the solution was added 30 g (0.12 mol) of iodine. Excess iodine is added to facilitate the 2,5-diiodo-3-methylthiophene. Diiodination of the 3-alkylthiophene monomer is a function of the reaction time as seen in Figure 3.1.

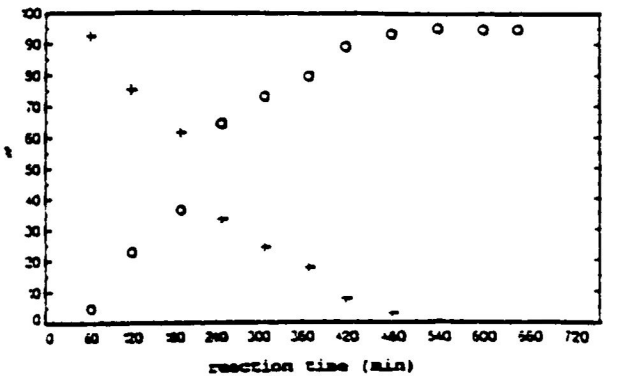


Figure 3.1 The formation of diiodinated 3-Akylthiophene as a function of the reaction time (+ = monoiodinated, o = diiodinated).

After refluxing for 3 hours under nitrogen gas, the organic was separated, washed with water (2 × 50 ml) , followed by 10% NaOH (3 × 50 ml) using a separatory funnel and water, then dried over $MgSO_4$. Next $MgSO_4$ is filtered out, and solvent is evaporated, distillation gave 20 g (56% yield) 2,5-diiodo-3-methylthiophene (b.p. 100+ °C at 7 mm Hg) NMR ($CDCl_3$ TMS): δ 6.85 (s 1H) δ 2.18 (s 3H).

Purification of Starting Materials

The purification of DIMT and DIOT were performed by stirring with overnight followed by distillation over CaH_2.

Tetrahydrofuran

Tetrahydrofuran (THF) (Fisher,certified) was purified by reflux under nitrogen and distillation from potassium and sodium alloy using benzophenone as an indicator.

Benzene

Benzene (Fisher certified) was purified by the same manner as THF.

Synthesis of 2,5 Diiodo-3-Octylthiophene

The synthesis of 2,5-diiodo-3-octylthiophene (DIOT) was prepared by iodination of 3-octylthiophene in CH2Cl2 using a 1:1 mixture of nitric acid and water as catalyst as described by method of Barker et. al. A 10 g (0.0508 mol) solution of 3-octylthiophene synthesized by method of Kumada et. al. in 150 ml of CH_2Cl_2 was placed in a 500 ml three-necked flask, to the solution was added 12.8 g of iodine crystals. A solution of 6 ml HNO_3 and H_2O is added to a dropping funnel and used to catalyze the reaction. After refluxing for 20 hours, the monomer is washed by the same method used in synthesizing 2,5-diiodo-3-methylthiophene. Distillation gives 11.3g 2,5-diiodo-3-octylthiophene (b.p. 140 °C at 2 mm Hg) NMR ($CDCL_3$ TMS): δ 6.88 (s 1H) δ 1.3 (s 2-6 H) δ 1.4(s 7 H) δ 2.46 (s 8 H) δ 0.9 (CH_3).

Synthesis of Octylthiophene

The octylthiophene used in the experiment was borrowed in the beginning, yet upon consumption it was found to be less expensive to synthesize in the laboratory by method Kumada et. al. via phosphino nickel complex catalyzed cross-coupling of Grignard reagents.

Procedure

In a 500 ml flask containing 1.5 g of Mg turnings, dried 24 hours under nitrogen, 100 ml of ethyl ether solvent is added. Afterwards, 1.5 ml octylbromide in 20 ml ethyl ether is added. The mixture is stirred at room temperature, until an exothermic reaction is observed. The flask can now be immersed in an ice water bath, and the rest of the 12 g of octylbromide in ether solution added over 1 hour. After refluxing for 30 minutes the

reaction is cooled to room temperature. Another 500 ml flask containing 0.12 g $NiCl_2$(dppp), 10.1 g Bromothiophene, and 150 ml ethyl ether is adjacent to the flask containing the Octyl-magnesium bromide reagent formed. The grignard reagent is transferred to the above mentioned vessel to complete the synthesis via a connecting syringe. Stirring and cooling in ice bath of the mixture as addition continues over 50 minutes is necessary. After 3 hours of stirring the mixture is refluxed with stirring for 6 hours, cooled in an ice bath, and cautiously hydrolyzed w/ aqueous 2 N HCl. The organic layer is next extracted with two 70 ml portions of ethyl ether and finally washed with water and sodium bicarbonate. Solvents are removed by drying over calcium chloride for 24 hours , followed by evaporation of remaining solvent, and distillation. A yield of 75+% was obtained for each synthesis of octylthiophene (b.p. 100 °C) δ 6.85 (s 1H) δ 2.85(s 2H) δ 1.2(s 12 H) δ 0.9 (s CH3).

Reagents

Ethyl Ether

Ethyl Ether (Fisher, certified) was purified by reflux and distillation from sodium and potassium benzophenone ketyl before use.

Bromooctane

Bromooctane was dried over MgSO4 for 24 hours then filtered and dried over P205, prior to being distilled and weighed out for use.

Bromothiophene

Bromothiophene was purified in the same manner as bromooctane.

Magnesium

Magnesium turnings were prepared by cutting strips of magnesium inot small pieces and drying for 24 hours under nitrogen stream inside the reaction vessel.

Polymerization of Poly[3-Octylthiophene-co-3-Methylthiophene]

The chemical route for polymerization of poly[3-Octylthiophene-co-3-Methylthiophene] referred to as P[3OT,3MT]. The 3-octylthiophene, 3-methylthiophene copolymers were polymerized using a nickel-phosphine catalyst. The procedure for the polymerization were by method of Li [77] in the synthesis of poly[3-methylthiophene] homopolymer, except both DIMT and DIOT were added. The significance of this polymerization was to gain experience at synthesizing copolymers, as well as, to characterize a random copolymer as a model prior to synthesizing the block copolymer. All polymers were synthesized under nitrogen atmosphere. Tetrahydrofuran and anisole, were dried by distillation from potassium sodium benzophenone ketyl just before use. Magnesium turnings (0.3524 g) were placed in a 100 ml three necked flask fitted with a reflux condenser, addition funnel and rubber septum stopper. The magnesium turnings were dried by heating overnight under a stream of nitrogen. After the flask cooled to room temperature, 50 ml of dry THF was added through the septum, as solvent and 3g (0.0066 mol) of DIOT and 3g (0.0085 mol) of DIMT were added dropwise via equalizing pressure addition funnel. the resulting mixture was refluxed for an additional 6 hours, this produced the grignard mixture. After most of the THF solvent was removed via evaporation, the residue was dissolved in 40 ml of purified anisole. Next, 0.04 g of NiCl2(dppp) , dissolved in anisole was added. The polymerization was allowed to proceed for 4.5 hours, producing a random copolymer of 3-octylthiophene and 3-methylthiophene. The polymerization was terminated by methanol. The copolymer was precipitated into hexanes, wash with methanol in a soxhlet extractor and finally dried in a

vacuum oven for one day at 60 °C. The polymer was then removed and washed with warm water to remove magnesium iodide salt.

Purification of starting materials

The purification of DIOT and DIMT monomers has been described.

ω-methoxyocta(oxyethylene)methacrylate

ω-methoxyocta(oxyethylene)methacrylate (MG8) (Polysciences Inc.) was purified by repeated azeotropic evaporation with benzene on a rotary evaporator. The macromonomer was again azeotropically dried three times with benzene and tetrahydrofuran, respectively, using high vacuum manifold techniques. The dried MG8 had THF added to form a solution which was stored in ampules equipped with breakseals.

Synthesis of P[3OT,3MT-B-MG8]

All polymerizations were carried out under dry nitrogen atmosphere. THF and anisole, were dried by distillation from potassium sodium benzophenone ketyl just before use.

Magnesium turnings (0.384 g) (98%) were placed into a 100 ml three-necked flask fitted with a reflux condenser, addition funnel and rubber septum stopper. The magnesium turnings were dried by heating overnight under a nitrogen stream. After flask cooled to room temperature, 50 ml of dry THF was introduced to the reaction vessel through the septum and 2g (0.004 mol) DIOT along with 4g DIMT were added dropwise via equalizing pressure funnel to the reaction vessel. The resulting mixture was refluxed for 5 hours. After most of the THF solvent was removed by evaporation, the residue was

dissolved in 40 ml of purified anisole. A solution of dry anisole and 0.04 g NiCl2 (dppp) dried under nitrogen gas was next added. The polymerization was allowed to proceed overnight; after which a small portion of solution is removed for NMR analysis, before adding MG8. An additional 0.04 g of $NiCl_2$ (dppp) is added to the reaction. The MG8 is next syringed in from a breakseal vessel and this polymerization is allowed to go overnight with little heating and then terminated with addition of methanol. The copolymer was precipitated into hexanes, washed with methanol in a soxhlet extractor and dried in a vacuum oven for 24 hours at 60 °C. The polymer was next washed in warm water to remove any magnesium iodide.

Apparatus

High-Vacuum Dual Manifold

The high vacuum manifold in Figure 3.1.1 is representative of the type used for all purification of MG8 macromonomer. A liquid nitrogen trap was used in order to prevent solvent vapors from entering the pumps as MG8 has a very high boiling point. Reaction vessels were connected to the high-vacuum line via high-vacuum three-way stopcocks. A reflux condenser was connected to the line for purification of the solvents. The absolute pressure of the vacuum system was measured by a McCleod vacuum gauge. Generally the vacuum provided by this system is 10^{-3} torr.

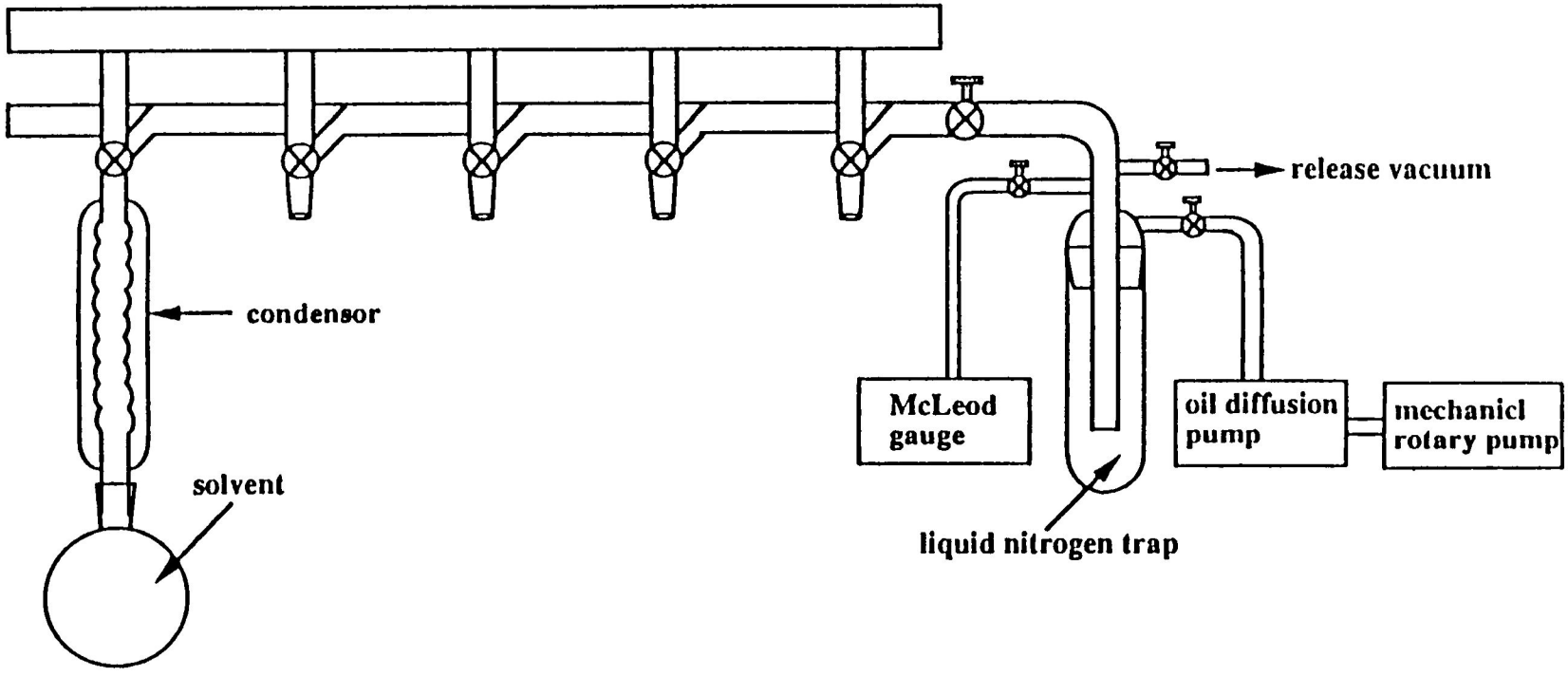


Figure 3.1.1 High Vacuum Manifold

Vessel for the Purification of ω-methoxyocta(oxyethylene)methacrylate (MG8)

The vessel used for purification of the MG8 macromonomer (shown in Figure 3.1.2) was designed from a 500 ml round bottom flask. Three ampules with break seals were connected to this flask for storage of the MG8 solution.

3.2 Preparation of Complexes of P[3OT,3MT-B-MG8]

Preparation of LiClO4 Salt Complexes

The complexes of P[3OT,3MT-B-MG8] were prepared by dissolving the 200 mg copolymers in 50 ml THF/Toluene followed by addition of a desired amount of LiClO4/THF solution with vigorous stirring for 24 hours at room temperature. the solvent was removed by suction evaporation. the complexes were dried in a vacuum oven for one day at 50 °C.

Doping of P[3OT,3MT-B-MG8] with FeCl3

P[3OT,3MT-B-MG8] (200 mg) was dissolved in CH_3NO_2/Toluene (85:15) and $FeCl_3$•6 H_2O was added. The mixture was stirred for 48 hours. The flask was next placed inside the vacuum drying oven for 24 hours to remove solvent and moisture from the polymer. The doping degree for all the polymer systems is 25% (1 $FeCl_3$: 4 Thiophene rings).

3.3 Characterization of Block Copolymers

Chemical and physical properties of P[3OT,3MT], P[3OT,3MT-B-MG8] and polymer intermediates were characterized by a variety of analytical techniques. Since most of the techniques are widely used in polymer characterization, only a brief

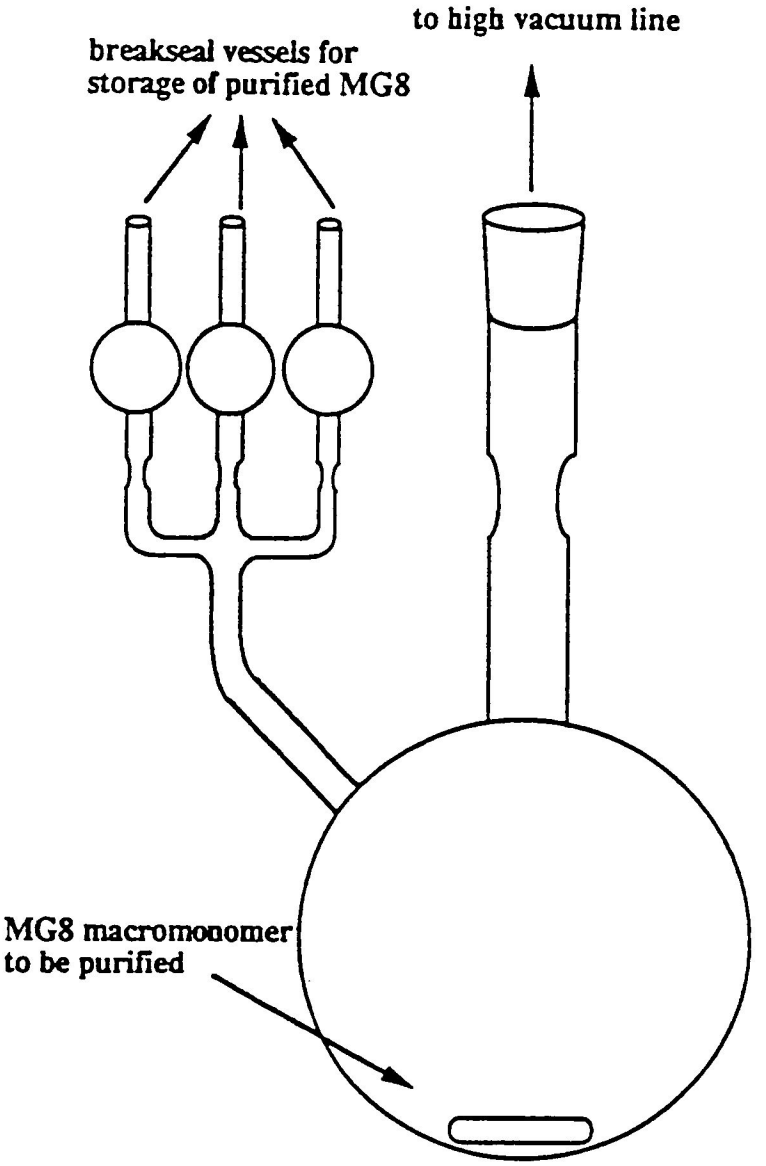


Figure 3.1.2 Vessel for purification of macromonomer MG8

description of the instruments employed and working conditions used is given. The techniques for conductivity measurement are discussed in more detail.

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) Routine ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WM 250 NMR spectrometer in $CDCl_3$. In all spectra analyzed Tetramethylsilane (TMS) was used as the internal standard. Solid State ^{13}C NMR was also used as a means of characterizing the block copolymers.

Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) of the copolymers was examined on a Perkin-Elmer DSC-4 equipped with a thermal data station. The test specimen was packed in an aluminum pan holder and scanned at a heating rate of 5 °C to 20 °C / minute under a nitrogen atmosphere. The sample was heated initially to 250 °C and quench cooled at a rate of 320 °C / minute to -70 °C before obtaining thermograms. The glass transitions were not clearly observable for these polymers, it is believed these polymers act as rigid rods and segmental motion may be undetectable by the DSC.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted for examination of stability of polymer samples. A model 951 Thermogravimetric Analyzer (Du Pont Instrument) interfaced to a 9900 computer (Du Pont Instrument) was used. The samples were packed in a platinum pan and then heated to the desired temperature at a heating rate of 5 °C/ minute under nitrogen atmosphere. The weight loss due to decomposition of the sample was recorded. The thermal stability of a sample was indicated as the decomposition temperature.

Gas Chromatography-Mass Spectrometry (GC-MS)

The verification of monomers was done by (GC-MS). The samples were prepared by dissolving unknown 2,5-diiodomethylthiophene into ethyl ether and injecting into the (GC-MS) instrument.

Transmission Electron Microscopy (TEM) The morphologies of the MIEC block copolymers were investigated by TEM. The specimens were prepared by embedding the polymer in epoxy and the epoxy was microtomed to 50 nm slices, these films were next cast onto copper grids and stained with OsO_4 for 1.5 weeks. The microscopy experiments were performed on an Hitachi 600 Transmission Electron Microscope operating at 75kV, provided by the Clark Atlanta Department of Biology.

Conductivity Measurements

Preparation of samples: All samples were dried in a vacuum oven at 60 °C for 24 hours prior to measuring conductivities. The required amount of samples were placed into a stainless steel pellet pressing apparatus and a Carver Laboratory Press was used to apply force about 6 metric tons.

Impedance Measurements:

Impedance measurements was performed as follows. A polymer pellet (13 mm diameter) between two copper electrodes was packed in a sealed cell under a dry nitrogen atmosphere. A small amount phosphorous pentoxide was placed on the bottom of the cell to protect the sample from moisture. A mineral oil bath equipped with a laboratory immersion heater provided heating and temperature control. The frequency dependence

of the samples were measured with an Hewlett-Packard 4912A Impedence Analyzer over a range of 5 Hz to 13 MHz.

The block copolymers form a two-phase microstructure. Taking this morphology into consideration, it was assumed that several components were present in this system; geometrical capacitance of the sample (Cg), bulk resistance (Rb), interfacial capacitance (Ci), and interfacial resistance (Ri) between the two phases. The equivalent circuit is shown in Figure 3.3.1. [75]

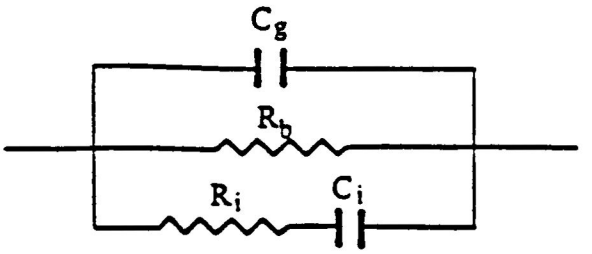


Figure 3.3.1 Equivalent Circuit for the Complex Impedance of the Copolymers

The frequency dependence of the impedance of the equivalent circuit is presented by

$$Z = \frac{R_b(I + i\omega C_i R_i)}{(I-\omega^2 C_g C_i R_b R_i) + i\omega(C_i R_i + C_i R_b + C_g R_b)}$$

Impedance is a complex quantitiy and consist of two components: a real compenent Z' and an imaginary Z". Z' and Z" are related to impedance Z by

$$Z = Z' + jZ"$$

The plot of the real part (Z') versus the imaginary part (Z") is the complex impedance diagram or the Cole-Cole plot. This diagram is characterized for polymer electrolytes by arcs. The bulk resistance of the ionic conducting polymer was derived from such diagram where the imaginary part of the impedance is zero.[77,78] The bulk resistance for the electronic conductivity was obtained from this diagram where the impedence and resistance did not change significantly with frequency in the low frequency range. The conductivity of a polymer sample was calculated from the bulk resistance according to the following equation

$$\sigma = D / A \times Rb$$

where σ is conductivity:

D is thickness of the sample;

A is section area of the sample;

Rb is bulk resistance.

Four-Point Probe Conductivity Measurement 79-81

The four-point probe technique is a suitable method for eliminating the interface resistance between the sample and electrode. The four-point probe apparatus is showing Figure 3.3.2. The four stainless-steel tips of the probe were individually spring loaded on a plastic base which was driven up or down by turning the handle of the slide screw. The probe tip force was not controlled by the holder but by the tension of the four individual springs inside the plastic base to ensure that the same force was exerted on the surface of the material by the tip.

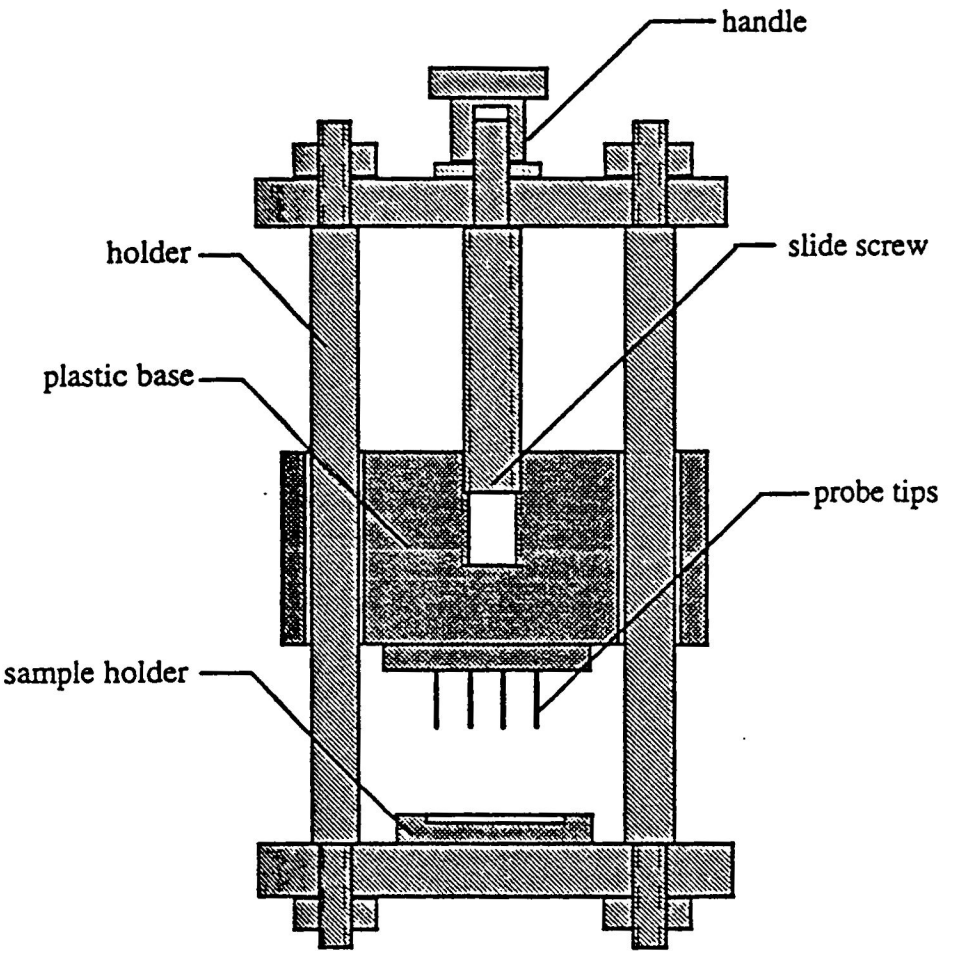


Figure 3.3.2 The Apparatus for Four-Point Probe Conductivity Measurement

The four-point probe apparatus was packed into a sealed cell and measurements were performed. The two inner tips connected to a multimeter (Fluke 79 Series II) to measure a potential difference between these probes ΔV); the two outer probes were connected to a power generator (Peschel Instrument Inc.) that supplied constant electrical current. The conductivity σ for a test sample using this method was calculated by following equation:

$$\sigma = R/2\ \pi\ d\ I$$

where sigma is conductivity; ΔV is potential difference: d is the space between the probe tips; I is the electrical current passed through the sample and R is the resistance.

Summary

The preceding chapters have provided the reader with an idea of the previously gained knowledge on research in the area of electroactive polymers. The next section shall contain an interpretation of the data gained from all new experiments which have lead to the completion of this project, a few published papers and a masters degree in polymer chemistry. There have been many hours put into the design of this project as shown throughout this thesis and yet many questions are yet to be answered. The reader is again urged to view the data carefully from an analytical frame of reference.

CHAPTER IV

RESULTS AND DISCUSSION

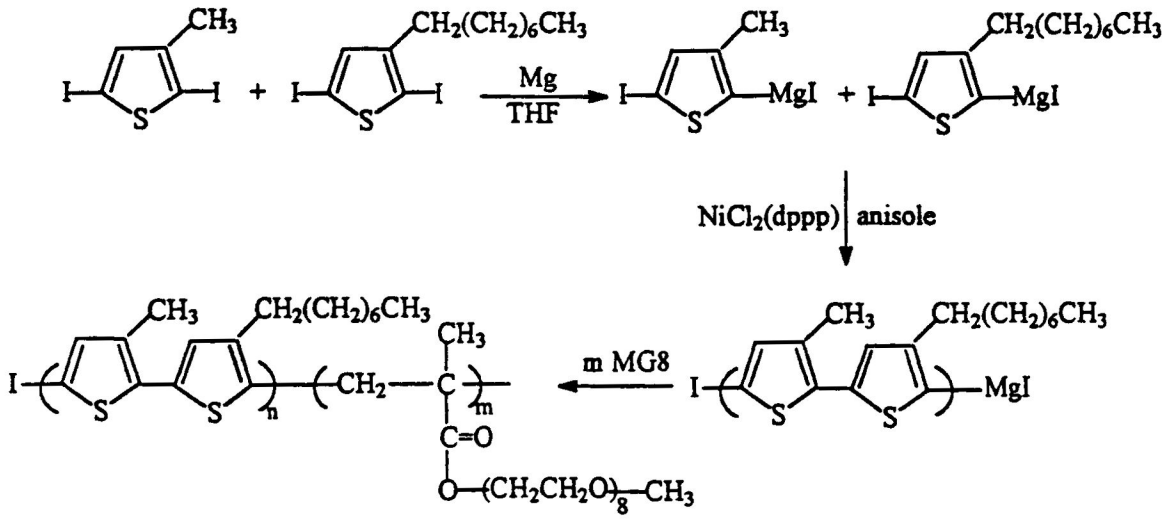
4.1 Synthesis and Properties of Poly[3-Octylthiophene-co-3-Methylthiophene-Block-ω-methoxyocta(oxyethylene)methacralyte]

Chemical Structure and Compositions of Copolymer

The synthesis of five P[3OT,3MT-B-MG8] block copolymers was completed via the chemical route shown in Scheme 1. The polymers are powdery materials which appear deep-reddish black in color. The polymers are slightly soluble in common organic solvents (THF, Toluene, etc.). These block copolymers are compression processable. The block copolymers were characterized by ^{13}C Solid State NMR spectroscopy. Figure 4.1.1 shows the ^{13}C NMR spectrum of 1:1 P[3OT,3MT-B-MG8], compared with the ^{13}C NMR of PEO and P[3MT-B-MG8] as a conformation for the polymer preparation. The bulk of the oxyethylene derivative of P[3OT,3MT-B-MG8] is seen at 75 ppm and the methylene carbons of the polymer are visible at 26 to 40 ppm.

The elemental analysis (Atlantic Microlab) of P[3OT,3MT-B-MG8] copolymers concluded numbers that were to low for justification initially; yet from reading the literature and performing melt temperature experiments on the polymer it was concluded that the reason for such low percentage composition was that MgI_2 from the thiophenyl grignard was still present in the polymer. Solvation and removal in warm water and methanol of the MgI_2, which has a solubility of 168 g/100 cc in solution, was

accomplished and confirmed by elemental analysis. The composition of elements in the polymer was dependent on weight fractions of monomer in the polymer which was unable to be completely determined as a result of inaccessibility to electron spray mass spectrometry and gel permeation chromatography instruments.



Scheme 1. Synthesis of P[3OT,3MT-MG8]

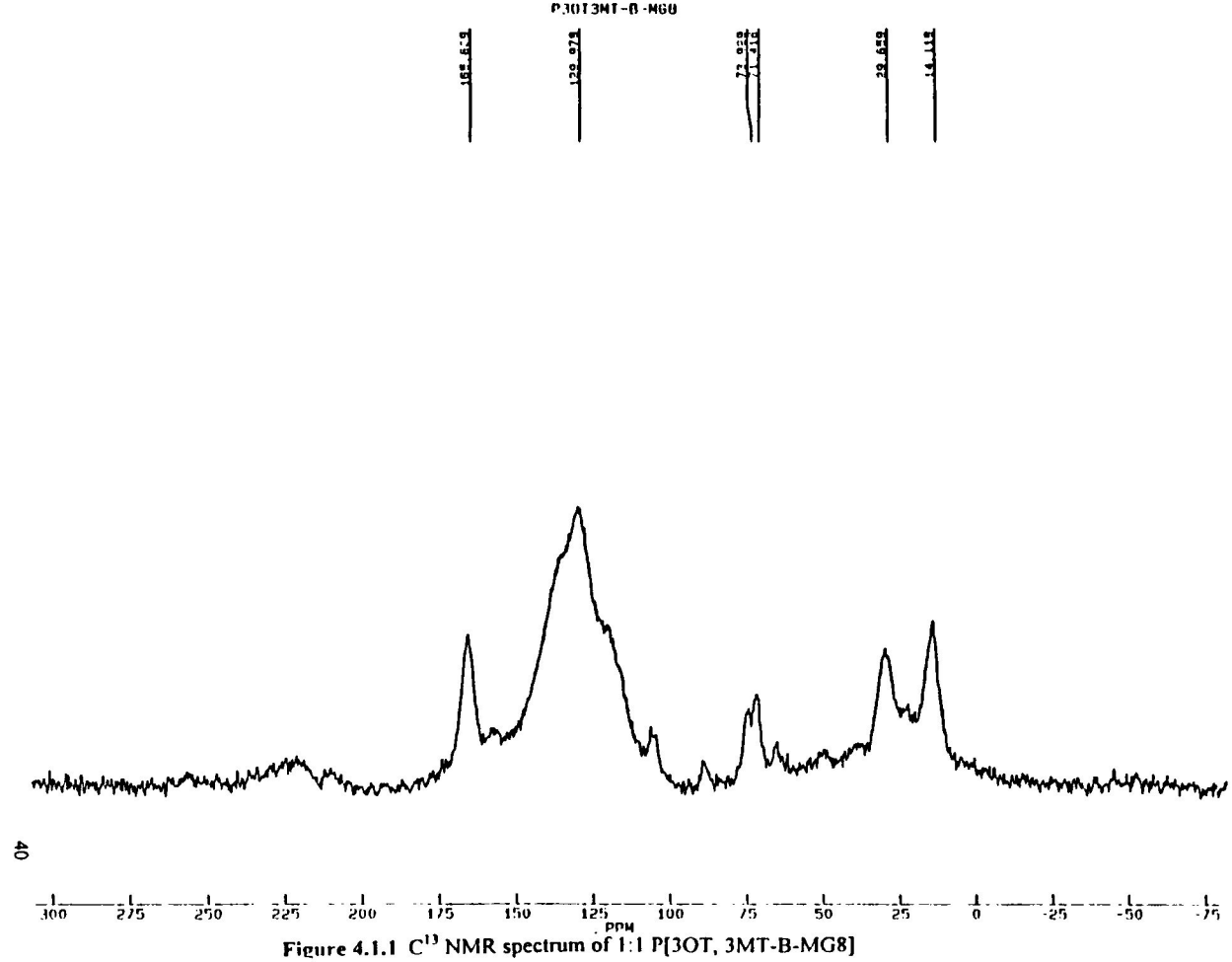


Figure 4.1.1 C^{13} NMR spectrum of 1:1 P[3OT, 3MT-B-MG8]

Also if the furnace used for elemental analysis incinerated the sample a ceramic may have been formed, thus distorting actual elemental composition. Inorganic analysis of the residue found 0 % Iodine, thus it was concluded, no MgI_2 was present; it was assumed the copolymer composition reflects the feed composition. Thermogravimetric analysis yielded 60 % residue at 300 °C, with this much residue at such temperatures accurate elemental analysis cannot be obtained. However, results obtained from elemental analysis experiments are summarized in Table 4.1.1.

Elemental Analysis Data
P[3OT, 3MT-B-MG8]

First Elemental Analysis

Ratio	% C	% H	% S
1: 3	26.07	4.87	4.68
3:1	31.74	4.38	8.24
2:1	30.03	4.64	4.81
Second Elemental Analysis			
1:3	29.23	4.85	
3:1	37.46	5.27	
2:1	35.54	6.46	
1:2	29.51	4.24	7.04
Third Elemental Analysis			
2:1	39.6	4.32	12.63
3:1	45.6	5.21	12.93

Table 4.1.1 Elemental Analysis Data for P[3OT, 3MT-B-MG8]

Thermal Properties Analysis

Thermal property studies were performed on the P[3OT,3MT-B-MG8] copolymers. DSC proved to be useless in detecting segmental motion of the block copolymers. Dynamic Mechanical Thermal Analysis studies were attempted because the instrument is more sensitive to onset of motion.. The samples further proved to be too brittle under the force of the DMA, which several orders of magnitude more sensitive to segmental motion of microdomains. It must be noted that it is not unusual to have difficulty determining Tg of the alkylthiophene homopolymers and copolymers. The glass transition of one of the precursors, poly(3-Octylthiophene-co-3-Methylthiophene) homopolymers is not observable by DSC and to the best of our knowledge a definitive glass transition for poly(3-methylthiophene) or poly(3-octylthiophene-co-3-methylthiophene) has not been reported.

The thermal stability of P[3OT,3MT-B-MG8] was examined by TGA. The samples were heated to 300 °C at a rate of 5 °C min-1 under a nitrogen atmosphere. The results can be seen in Figure 4.1.2.

The conclusion was reached that the copolymers are stable up to 285 °C, where more than half of the weight is retained.

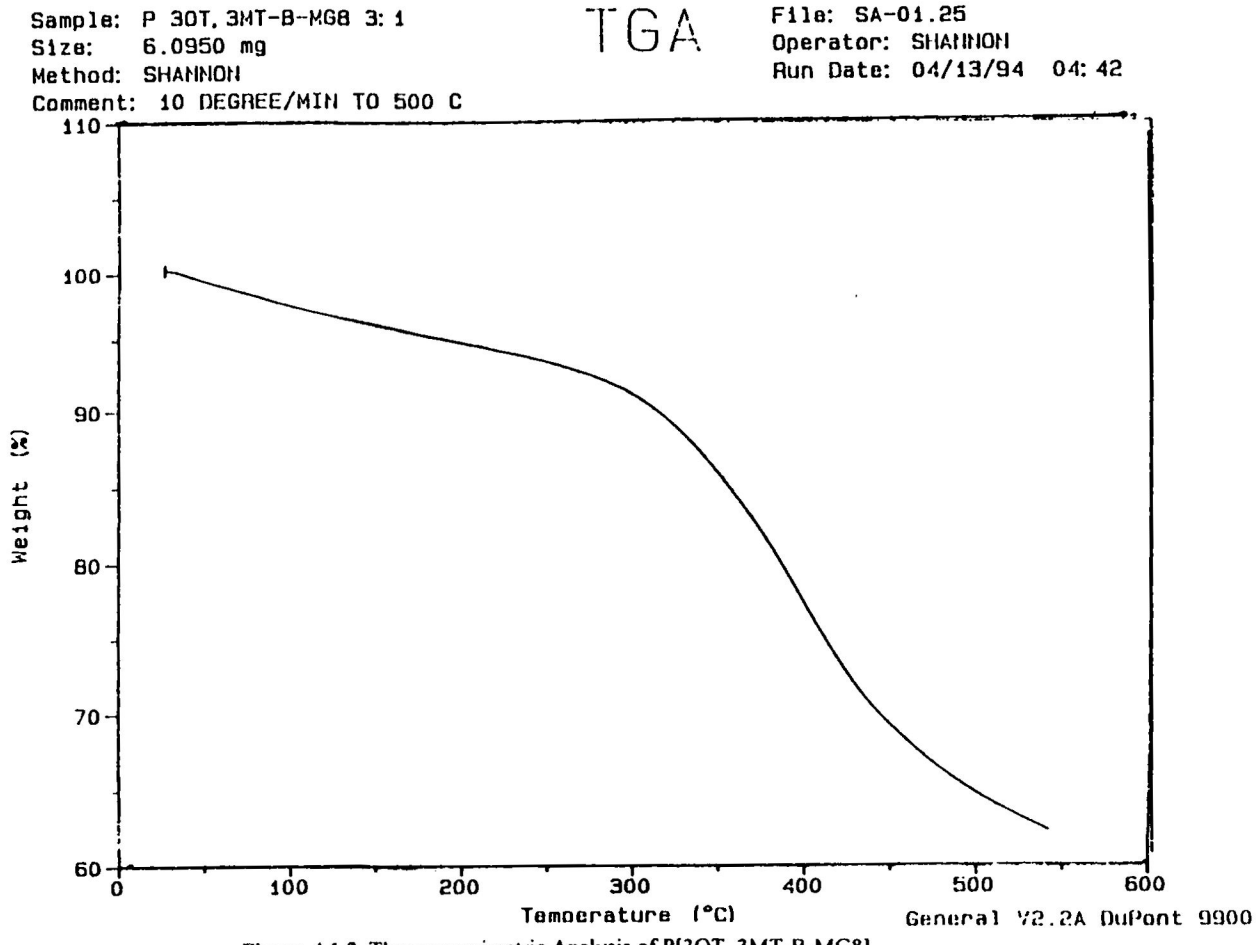


Figure 4.1.2 Thermogravimetric Analysis of P[3OT, 3MT-B-MG8]

Microstructure of Electroactive Block Copolymers

Transmission electron micrographs of epoxy embedded copolymers possessing different electronic and ionic feed rations are shown in Figure 4.1.3. The samples appear lamella under TEM operating at 75 kV and 25 - 35 $\times$ 10^3 magnification. In most micrographs the electronic conducting phase is adjacent to the ionic conducting phase, which appears lighter in contrast. It is important to note that OsO4 is known to stain block copolymers, and unsaturated hydrocarbons.[82]

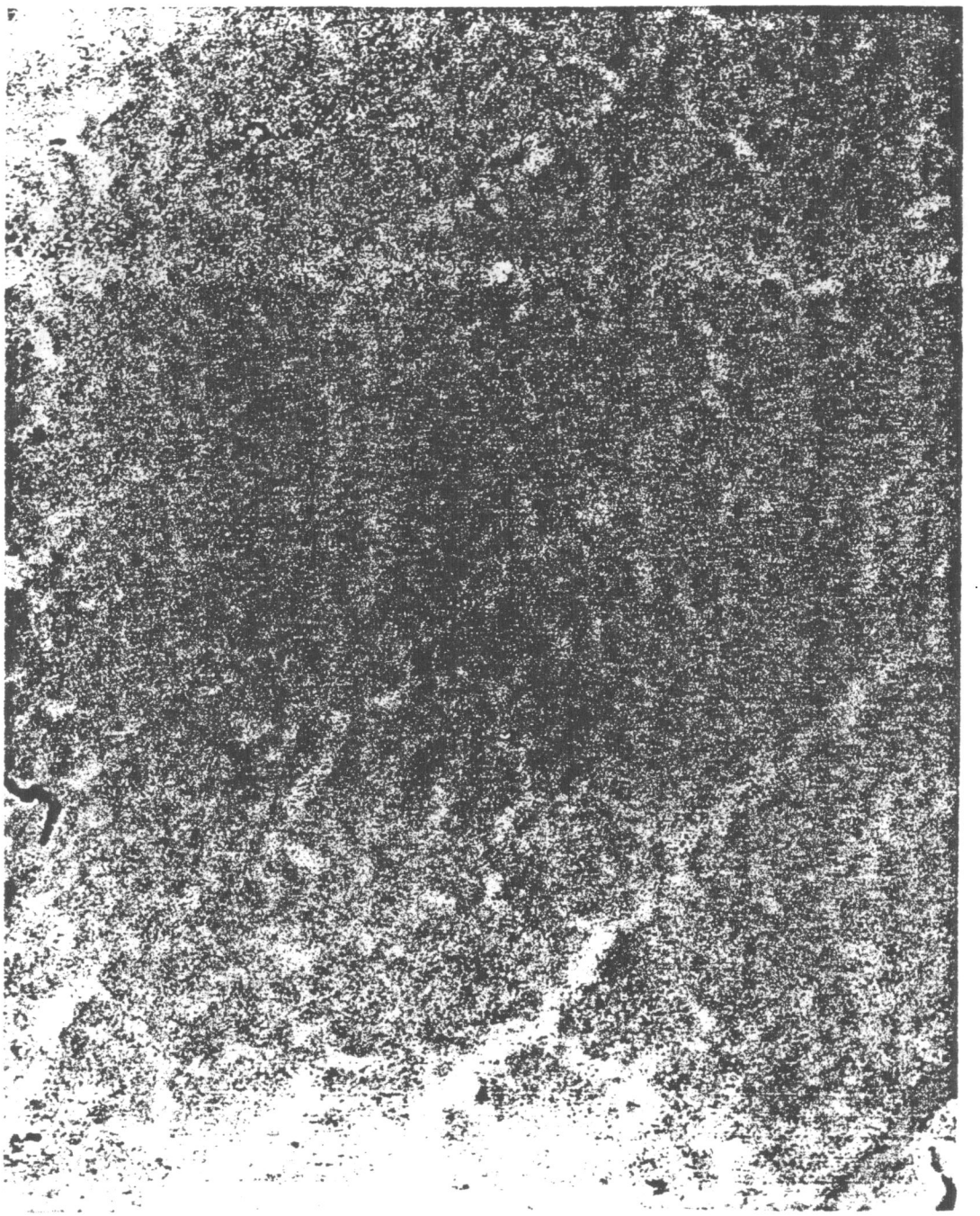


Figure 4.1.3 TEM micrograph of 3:1 P[3OT,3MT-MG8] depicting ionic and electronic domains.

Ionic Conductivities of LiClO4 Complexes

Ionic conductance was obtained by impedance analysis.

The maximum conductance value obtained was 5.1×10^{-5} at room temperature.

Electronic Conductivities of P[3OT,3MT-B-MG8] copolymer with $FeCl_3$ Dopant

Four probe technique was incorporated for determination of electronic conductivities of the 25 % $FeCl_3$ doped P[3OT,3MT-B-MG8] block copolymers. The results of the measurement at ~ 25 % doping level (1 $FeCl_3$/ 4 3-alkyl-thiophene rings) are shown in Table 4.1.2. The electronic conductivity for these systems range from 10^{-4} s cm-1 to 10^{-2} S cm-1 occuring for 1:1 P[3OT,3MT-B-MG8]. The low conductivity can be attributed to the presence of a non-electron conductive matrix. All obtained values are consistently higher than the ionic conductance values received. Both sets of values are acceptable considering presence of a different conducting phase in the matrix to ion/electron flow.

COMPOSITION (WT %)			CONDUCTIVITY (σ) ($S\ cm^{-1}$)
3MT	3OT	MG8	ELECTRONIC
60	20	20	4.2×10^{-3}
50	25	25	1.3×10^{-2}
33	33	34	4.8×10^{-2}
20	40	40	2.4×10^{-2}
20	60	20	3.5×10^{-2}

Table 4.1.2 Compositions and Electronic Conductivities of P[3OT,3MT-B-MG8] Block Copolymers

CONCLUSION

A series of microphase separated mixed (electronic and ionic) conducting block copolymers (i.e. P[3OT, 3MT-B-MG8]) have been prepared. It is evident from electron microscopy that the series of block copolymers form a phase separated microstructure.

The P[3OT, 3MT-B-MG8] block copolymers are both electronic and ionic conductiver. The 3-octylthiophene-3-methylthiophene copolymer block has been doped at 25% doping level (1 $FeCl_3$ / 4 Thiophene Rings), to obtain an electronic conducting domain. The oligooxyethylene block was doped with $LiClO_4$ to obtain the ionic conducting domain. The copolymer upon doping exhibits electronic conductivities and ionic conductivities that are higher than those possessed by P[3MT-B-MG8] and upon complete removal of MgI_2 inorganic residue as revealed byelemental analysis the polymer exhibits even higher conductivities. All electronic conductivities obtained are greater than resulting ionic conductivities. The polymer is thermally stable up to 285 °C.

The conductivity differences and stability of the polymers make them desirable for biomedical, and nano- and microscale electrochemical applications. The electronic conductivities are highest where 3-octylthiophene is highest in concentration. It is evident that by altering chemical structure, the polymer can be made to take on new properties, including higher electronic conductivity, and melt processibility. I would suggest that a

polymer of P[3OT-B-MG8] be synthesized. This would be a facile polymer synthesis since the less expensive synthesis of octylthiophene has carried out in our lab, and shown to be purer than the the expensive octylthiophene purchased from TCI America. It would be interesting to look at ionic concuctance in an magnetic field. The previously synthesized systems as well as the suggested polymers would be ideal at meeting demand for highly conductive, enviromentally stable, processable application materials.

The possibility for devices and improvement in existing technologies using microphase separated mixed ionic and electronic conducting block copolymers is very broad. We have suggested devices such as switches, solid state sensors, membranes for ionorganic/biological electron transfer, and electromagnetic interference shields. The biological application of this type of polymer is very significant in that if the polymer can be made biocompatible they may be used for synthetic membranes.

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